



# Catalytic oxidation and adsorption of $\text{Hg}^0$ over low-temperature $\text{NH}_3$ -SCR $\text{LaMnO}_3$ perovskite oxide from flue gas



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## ABSTRACT

To simultaneously remove elemental mercury ( $\text{Hg}^0$ ) and  $\text{NO}_x$  at low temperature from flue gas in coal-fired power plants, an efficient  $\text{NH}_3$ -SCR  $\text{LaMnO}_3$  perovskite oxide was chosen as the catalyst for  $\text{Hg}^0$  removal. The physicochemical properties, surface reaction and mercury desorption were investigated using BET, XRD, XPS,  $\text{H}_2$ -TPR and  $\text{Hg}$ -TPD, to investigate the  $\text{Hg}^0$  capture mechanism over  $\text{LaMnO}_3$  oxides. The results indicated that  $\text{LaMnO}_3$  exhibits a  $\text{Hg}^0$  capacity that is as high as 6.22 mg/g (600 min) at 150 °C.  $\text{O}_2$  enhanced the  $\text{Hg}^0$  removal performance by re-oxidation of reduced  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  and providing additional adsorbed oxygen.  $\text{NO}$  enhanced the  $\text{Hg}^0$  removal performance. However,  $\text{NH}_3$  exhibited negative effects on  $\text{Hg}^0$  removal. The  $\text{NH}_3 + \text{O}_2$ -TPD and  $\text{NO} + \text{O}_2$ -TPD results indicated that the ad- $\text{NH}_3$  species prevent  $\text{Hg}^0$  adsorption, but the ad- $\text{NO}_2$  species were beneficial for  $\text{Hg}^0$  oxidation. The effects of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  were also investigated, and the results indicated that they inhibited  $\text{Hg}^0$  removal.  $\text{Hg}$ -TPD under different reaction atmospheres was employed to further investigate the combining state of  $\text{Hg}^0$  on  $\text{LaMnO}_3$  surface, the results indicated that mercury primarily existed as  $\text{Hg}-\text{O}$ , and  $\text{LaMnO}_3$  can be regenerated using thermal desorption.

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## 1. Introduction

Elemental mercury ( $\text{Hg}^0$ ) in the atmosphere is hazardous for human and the environment [1–3]. The Minamata Convention on Mercury signed aiming at controlling mercury emission globally. Among the various emission sources, coal-fired power plants are major anthropogenic mercury emission sources [4,5]. In China, approximately 38% of the  $\text{Hg}^0$  is emitted from coal-fired flue gas [5]. Currently,  $\text{Hg}^0$  removal technologies are often part of the available equipment for co-beneficial mercury control (e.g., using SCR catalysts for the oxidation of  $\text{Hg}^0$  to oxidized mercury ( $\text{Hg}^{2+}$ ), followed by  $\text{Hg}^{2+}$  removal in wet flue gas desulfurization (WFGD) system) [6–8]. Another method was adsorption technology, and activated carbon injection (ACI) technology makes full use of AC to adsorb  $\text{Hg}^0$ . In addition, the particle-bound mercury ( $\text{Hg}^p$ ) is removed along with fly ash in the ESP/FF system [9,10]. However, the  $\text{Hg}^{2+}$  enriched in the WFGD system or mercury in the fly ashes could cause secondary mercury contamination [7,11]. Furthermore, the use of the ACI technology was limited due to its high cost, depen-

dences on the type of coal, inlet mercury concentration and reaction temperature [12,13].

In addition, more strict regulation aims to approach zero emission in coal-fired power plants, and the emission concentration should be  $\text{NO}_x \leq 5 \text{ mg/m}^3$  and  $\text{Hg}^0 \leq 0.002 \text{ mg/m}^3$ . However, in many coal-fired power plants, the space required for the installation of  $\text{deNO}_x$  unit that operate at flue gas temperature of 350–400 °C is insufficient. To avoid deactivation of SCR catalyst and reduce costs, the proposed additional  $\text{deNO}_x$  technologies could be loaded downstream of the particle control devices where the flue gas temperature is lower than 200 °C. However, traditional SCR catalysts ( $\text{V}-\text{W}-\text{TiO}_2/\text{V}-\text{Mo}-\text{TiO}_2$ ) may lose their activity at this low temperature. Moreover, without SCR catalysts in the coal-fired power plants,  $\text{Hg}^0$  is difficult oxidized to  $\text{Hg}^{2+}$  [14,15]. Therefore, to simultaneously remove  $\text{NO}_x$  and  $\text{Hg}^0$ , the low-temperature  $\text{deNO}_x$  technology along with  $\text{Hg}^0$  capture needs to be improved.

In previous studies, low-temperature  $\text{NH}_3$ -SCR technology had been widely studied and appears to be a potential method for  $\text{NO}$  removal. Many transition metal oxides such as  $\text{MnO}_x$ ,  $\text{FeO}_x$ ,  $\text{V}_2\text{O}_5$ , and  $\text{CoO}_x$  have been employed as catalysts for  $\text{NO}$  removal [16–19]. Mn-based oxides attracted much attention for capturing  $\text{Hg}^0$  due to their high redox potential, low cost and environmental friendliness [20]. The valance state of Mn and the existing state of O are important for the removal of  $\text{Hg}^0$ . During the  $\text{Hg}^0$  removal process,

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Hg<sup>0</sup> oxidized to Hg<sup>2+</sup> on the surface of MnO<sub>x</sub>, followed by reduction of high valance Mn<sup>4+</sup> to Mn<sup>3+</sup> or Mn<sup>2+</sup>. Then the oxidized mercury exists as Hg–O on the surface of the Mn-based materials. Among various Mn-based low-temperature NH<sub>3</sub>-SCR catalysts, perovskite type Mn-based oxides have recently attracted growing interest as alternative catalysts due to their low cost, high catalytic activity and strong thermal stability [21–25]. The general chemical formula for perovskite oxide is ABO<sub>3</sub>, in which the A ions can be rare earth and alkaline ions, and the B ions are often first-row transition metal ions. The catalytic properties are primarily due to the abnormal valence of the B ion, which is induced by the electric neutrality principle. The Mn ions can occupy the B site of perovskite oxides. The abundance of adsorbed oxygen and the oxygen valance may result in Hg<sup>0</sup> oxidation. LaMnO<sub>3</sub> exhibited a higher catalytic oxidation performance than that of other Mn-based perovskite oxides. In addition, LaMnO<sub>3</sub> had been used as low-temperature catalyst for NO removal. However, there was still no attempt for the catalytic oxidation of Hg<sup>0</sup> using NH<sub>3</sub>-SCR catalysts.

Herein, LaMnO<sub>3</sub> perovskite oxides were synthesized for the removal of Hg<sup>0</sup>. A fixed-bed reaction system was constructed to investigate the Hg<sup>0</sup> removal performance. The effects of O<sub>2</sub>, NH<sub>3</sub>, NO, H<sub>2</sub>O and SO<sub>2</sub> flue gas components were considered in our study and the mechanism for Hg<sup>0</sup> capture under different gas components is discussed. Furthermore, the mercury desorption performance was also investigated in our study.

## 2. Experimental

### 2.1. Catalyst preparation

The LaMnO<sub>3</sub> catalysts were prepared using a sol-gel method. Briefly, the required amount of La(NO<sub>3</sub>)<sub>3</sub> and Mn(NO<sub>3</sub>)<sub>3</sub> was dissolved in diluted water, followed by the addition of citric acid (CA) to the mixture. The temperature of the aqueous solution was maintained at 80 °C. The molar ratio of La:Mn:CA was 1:1:2. After vigorous stirring and evaporation, a transparent gel was formed, which was dried at 100 °C overnight. The obtained precursor was calcined at 300 °C for 1 h in air to completely decompose citric acid followed by calcination at 750 °C for 5 h at a rate of 10 °C/min. For comparison, MnO<sub>x</sub> and LaO<sub>x</sub> were also synthesized according to the same sol-gel method.

### 2.2. Physical characterization

The materials were characterized and analyzed using various techniques. The crystallinity of the fresh samples were determined by X-ray diffraction (XRD, APLX-DUO, BRUKER, Germany) on with Cu-Kα radiation. The XRD patterns were recorded in a 2θ range from 10° to 80° at a scanning rate of 5°/min. The multipoint Brunauer–Emmett–Teller (BET) surface was analyzed using a N<sub>2</sub> sorption measurement (Nova-2200 e) at 77 K. The pore diameter and pore volume were calculated based on the Barrett–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS, Shimadzu–Kratos) was used to examine the valance states of the elements on the surface of the materials. This instrument coupled with an ultra DLD spectrometer with an Al Kα excitation source. The C 1s line at 284.6 eV was employed as a reference for the binding energy calibration. The morphology and structure of as-prepared materials were observed via a transmission electron microscopy (TEM), and the images were using a JEOLJEM-2010 TEM electron microscope operating at 200 kV. The reducibility of the samples was determined using H<sub>2</sub>-TPR experiments, and these experiments were performed on a Chemisorp TPx 290 instrument. The samples were degassed at 200 °C for 3 h under

an Ar atmosphere prior to the tests, and the reducing gas consisted of 10% H<sub>2</sub>/Ar.

NH<sub>3</sub> + O<sub>2</sub> and NO + O<sub>2</sub>-temperature programmed desorption (NH<sub>3</sub> + O<sub>2</sub>-TPD and NO + O<sub>2</sub>-TPD) was performed using the fixed-bed adsorption system shown in Fig. 1. A FT-IR gas analyzer was employed to detect the gas components along with the increase in temperature. 20 mg of each sample was pre-treated by 500 ppm NH<sub>3</sub> + 4% O<sub>2</sub> (for NH<sub>3</sub> + O<sub>2</sub>-TPD) and 500 ppm NO + 4% O<sub>2</sub> (for NO + O<sub>2</sub>-TPD) at 50 °C, until the NH<sub>3</sub> or NO concentration did no change. NH<sub>3</sub> + O<sub>2</sub> and NO + O<sub>2</sub> were balanced with pure N<sub>2</sub> (total flow rate = 500 ml/min). Then, the fixed-bed temperature was increased at a rate of 10 °C/min and NO, NH<sub>3</sub>, N<sub>2</sub>O and NO<sub>2</sub> were detected and recorded using a FT-IR gas analyzer.

### 2.3. Hg<sup>0</sup> removal tests

The Hg<sup>0</sup> removal activities were evaluated using a fixed-bed reactor, and a schematic representation of the Hg<sup>0</sup> adsorption system is shown in Fig. 1. An Hg<sup>0</sup> permeation tube was used to generate Hg<sup>0</sup> vapor carried by pure N<sub>2</sub>, which was introduced to the inlet of the gas mixer. Other gases including NO, O<sub>2</sub>, SO<sub>2</sub>, and H<sub>2</sub>O vapor were introduced to the gas mixer at constant flow rates. NH<sub>3</sub> was separately introduced into the simulated flue gas. The flow rate was controlled by mass flow controllers (MFC) and the total flow rate was set to 200–500 ml/min. A fixed-bed reactor system was used to investigate the Hg<sup>0</sup> adsorption performance. The reaction temperature was controlled from 50 to 350 °C by a temperature controller tubular furnace. A cold vapor atomic absorption spectroscopy (CVASS) analyzer was employed as an online continuous detector that could only detect Hg<sup>0</sup>. The concentration of Hg<sup>0</sup> was measured using Lumex RA 915+. The inlet concentration of Hg<sup>0</sup> was 100–500 μg/m<sup>3</sup>. At the beginning of each test, the simulated gas bypassed the reactor and the inlet gas was detected to ensure a stable Hg<sup>0</sup> concentration. Then the simulated gas passed the samples and the Hg<sup>0</sup> concentration was detected by CVASS online system.

The Hg<sup>0</sup> removal efficiency and adsorption capacities were calculated according to Eqs. (1) and (2):

$$\eta = \frac{Hg_{in}^0 - Hg_{out}^0}{Hg_{in}^0} \quad (1)$$

$$Q = \frac{1}{m} \int_{t_0}^{t_1} \left( \frac{Hg_{in}^0 - Hg_{out}^0}{Hg_{in}^0} \right) \times f \times dt \quad (2)$$

$$NO \text{ removal efficiency} = \frac{NO_{in} - NO_{out}}{NO_{in}} \quad (3)$$

where  $\eta$  is the Hg<sup>0</sup> removal efficiency,  $Hg_{in}^0$  is the inlet concentration of Hg<sup>0</sup>,  $Hg_{out}^0$  is the outlet concentration of Hg<sup>0</sup>,  $Q$  is the Hg<sup>0</sup> adsorption capacity,  $m$  is the mass of the sorbent in the fixed-bed,  $f$  is the flow rate of the influent, and  $t_0$  and  $t_1$  are the initial and final test times, respectively, of the breakthrough curves.

### 2.4. NH<sub>3</sub>-SCR catalytic activity measurement

The NH<sub>3</sub>-SCR experiments were also performed in a fixed bed system. The experiments were performed according to the procedures employed in the Hg<sup>0</sup> adsorption tests. 20 mg sample was inserted into the reactor under an atmosphere consisting of 500 ppm NH<sub>3</sub>, 500 ppm NO and 4% O<sub>2</sub>, which was balanced by N<sub>2</sub>, at a total flow rate of 500 ml/min. The temperature ranged from 100 to 300 °C. The FT-IR gas analyzer was employed to detect the gas component in the outlet of the flue gas.

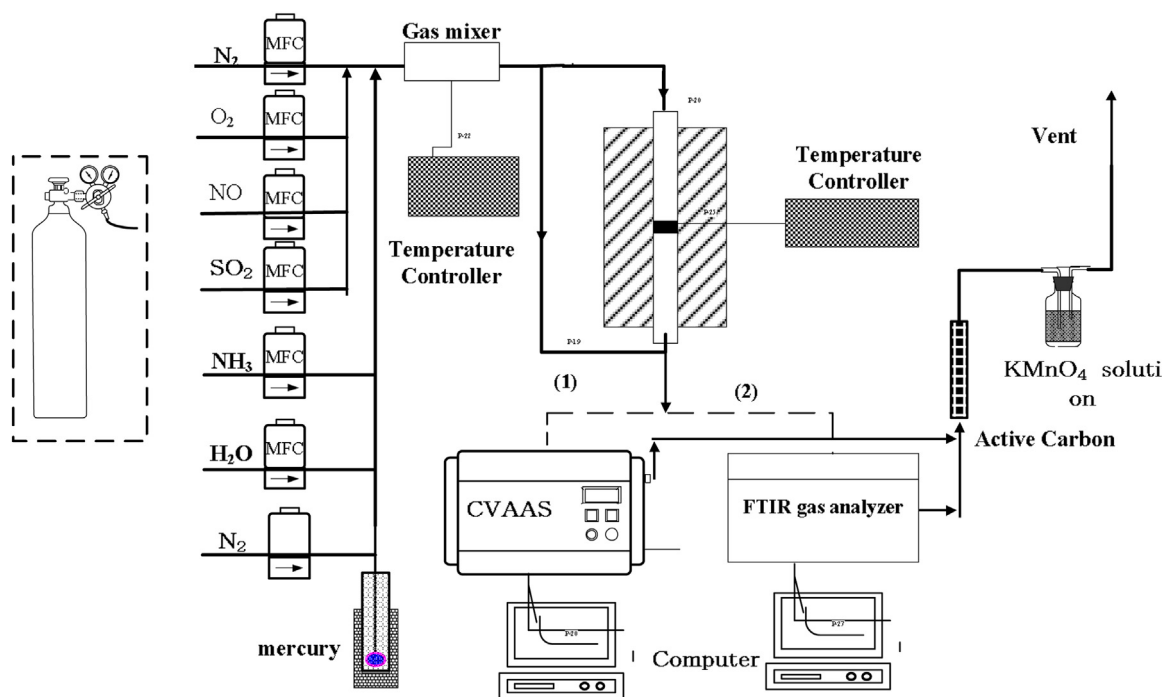


Fig. 1. Flow process of  $\text{Hg}^0$  adsorption and the  $\text{NH}_3$ -SCR assessment system.

## 2.5. Regeneration measurement

The mercury temperature programmed desorption (Hg-TPD) method was developed to evaluate the desorption performance of  $\text{LaMnO}_3$ . Prior to each test, the sorbents were adsorbed for 20 min at 150 °C with  $\text{N}_2$  (for  $\text{N}_2 + \text{Hg}$ -TPD), 4%  $\text{O}_2$  (for  $\text{O}_2 + \text{Hg}$ -TPD), 4%  $\text{O}_2 + 500 \text{ ppm NH}_3$  (for  $\text{O}_2 + \text{NH}_3 + \text{Hg}$ -TPD), 4%  $\text{O}_2 + 500 \text{ ppm NO}$  (for  $\text{O}_2 + \text{NO} + \text{Hg}$ -TPD) and 4%  $\text{O}_2 + 500 \text{ ppm SO}_2$  (for  $\text{O}_2 + \text{SO}_2 + \text{Hg}$ -TPD). After the furnace cooled to 100 °C, the sorbents were regenerated by heating from 100 to 700 °C in a pure  $\text{N}_2$  carrier gas. The heating rates were set to 2, 5 and 10 °C/min. The mercury signal was recorded by a CVAAS online system.

## 3. Results and discussion

### 3.1. Physicochemical properties

Fig. 2 shows the XRD patterns of the  $\text{LaO}_x$ ,  $\text{MnO}_x$  and  $\text{LaMnO}_3$  samples. For the  $\text{LaO}_x$  samples, the peaks were assigned to the  $\text{La}(\text{OH})_3$  diffraction pattern (JCPDS 83-2034) and  $\text{La}_2\text{O}_3$  diffraction pattern (JCPDS 05-0602) [26]. For  $\text{MnO}_x$ ,  $\text{Mn}_2\text{O}_3$  (JCPDS 24-0508) was the primary phase, and only a few peaks were ascribed to other crystalline manganese oxides. However, for  $\text{LaMnO}_3$ , the peaks were located at 22.8, 32.6, 40.2, 46.7, 52.8, 58.1, 68.3 and 77.8°, and all of these characteristic peaks can be well indexed to a perovskite phase (PDF-88-0633) with a rhombohedral structure.

The  $\text{N}_2$  adsorption–desorption isotherms and pore size distributions of  $\text{LaMnO}_3$  were investigated, and the results are shown in Table 1. The BET surface area of the prepared  $\text{LaMnO}_3$  was

**Table 1**  
Textural properties (BET surface area, pore volume and pore diameter) of the as-prepared samples.

Materials	BET surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore diameter (nm)
$\text{La}_2\text{O}_3$	2.3	0.068	3.34
$\text{MnO}_x$	11.2	0.051	3.30
$\text{LaMnO}_3$	16.6	0.118	11.5

16.6  $\text{m}^2/\text{g}$ , and the total pore volume and average pore diameter were 0.118  $\text{cm}^3/\text{g}$  and 11.5 nm, respectively. For comparison, the BET surface areas of  $\text{La}_2\text{O}_3$  and  $\text{MnO}_x$  were also calculated. The BET surface area of  $\text{La}_2\text{O}_3$  was 2.3  $\text{m}^2/\text{g}$ , which was smaller than that of  $\text{LaMnO}_3$ , and the pore volume was 0.068  $\text{cm}^3/\text{g}$ , which was also smaller than that of  $\text{LaMnO}_3$ . For  $\text{MnO}_x$ , the BET surface area was 11.2  $\text{m}^2/\text{g}$ , and the pore volume and pore diameter were 0.051  $\text{cm}^3/\text{g}$  and 3.308 nm, respectively. To further elucidate the textural properties of  $\text{LaMnO}_3$ , the TEM image is shown in Fig. S1, the uniform crystal lattice was indicative of the perovskite structure. In addition, the EDS analysis indicated that the elemental components were La, Mn and O.

Nest, the valance states of the elements were characterized by XPS. The results are reported in Fig. 3(a). For the Mn 2p spectrum of  $\text{LaMnO}_3$ , the peaks at 643.7 and 641.7 eV were correspond to  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$ , respectively [27]. The ratio of  $\text{Mn}^{4+}/\text{Mn}^{3+}$  was determined to be 33.93/66.07. A higher valence state of Mn may result in a higher catalytic oxidation activity [28,29]. The state of O was also evaluated by XPS analysis, as shown in Fig. 3B, in the O 1s spectrum of  $\text{LaMnO}_3$ , the peaks located at 531.0 and 529.6 eV were ascribed to the lattice oxygen ( $\text{O}_{\text{latt}}$ ) and adsorbed oxygen ( $\text{O}_{\text{ads}}$ ), respectively [30]. The ratio of  $\text{O}_{\text{latt}}/\text{O}_{\text{ads}}$  was approximately 47.51/52.49 in the fresh samples. The adsorbed oxygen was favorable for  $\text{Hg}^0$  capture [29,31].

### 3.2. $\text{Hg}^0$ removal over $\text{NH}_3$ -SCR $\text{LaMnO}_3$ perovskite oxide

#### 3.2.1. $\text{NH}_3$ -SCR performance over $\text{LaMnO}_3$

$\text{LaMnO}_3$  has been previously used as a low-temperature  $\text{NH}_3$ -SCR catalyst for NO removal from coal-fired flue gas [32]. As shown in Fig. 4(a), the  $\text{NH}_3$ -SCR performance of  $\text{LaO}_x$ ,  $\text{MnO}_x$  and  $\text{LaMnO}_3$  were tested.  $\text{LaO}_x$  exhibited almost no activity for NO removal.  $\text{MnO}_x$  exhibited a NO conversion of approximately 20% at 250 °C. However, for  $\text{LaMnO}_3$ , the NO conversion was higher than 65% at 200 °C. When the temperature increased from 250 to 350 °C, the NO conversion efficiency decreased. The Mn-based materials lost their activity for NO conversion at higher temperature (>200 °C). This

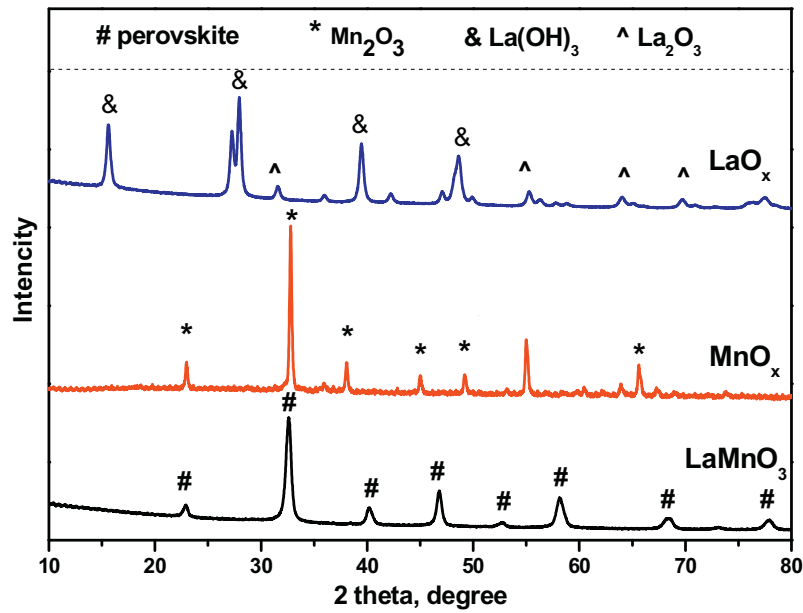


Fig. 2. XRD patterns of the  $\text{LaO}_x$ ,  $\text{MnO}_x$  and  $\text{LaMnO}_3$  samples.

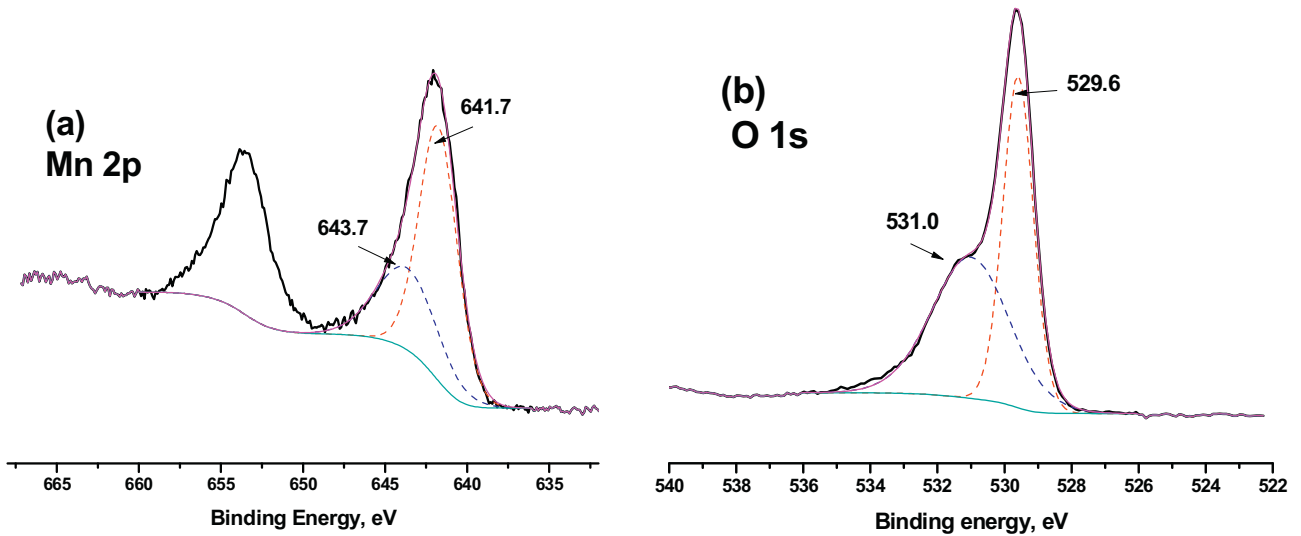


Fig. 3. XPS spectra of fresh  $\text{LaMnO}_3$  over the spectral regions of (a) Mn 2p and (b) O 1s.

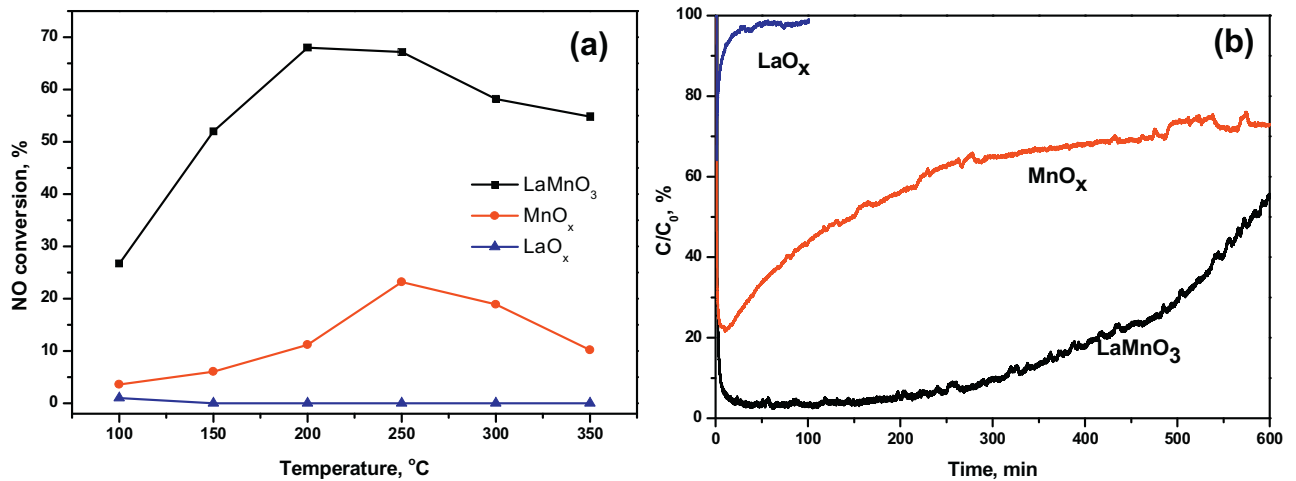


Fig. 4. Performance of (a) NO conversion and (b)  $\text{Hg}^0$  removal over  $\text{LaO}_x$ ,  $\text{MnO}_x$  and  $\text{LaMnO}_3$ ; Reaction condition: GHSV =  $478,000 \text{ h}^{-1}$  and 4%  $\text{O}_2$ .

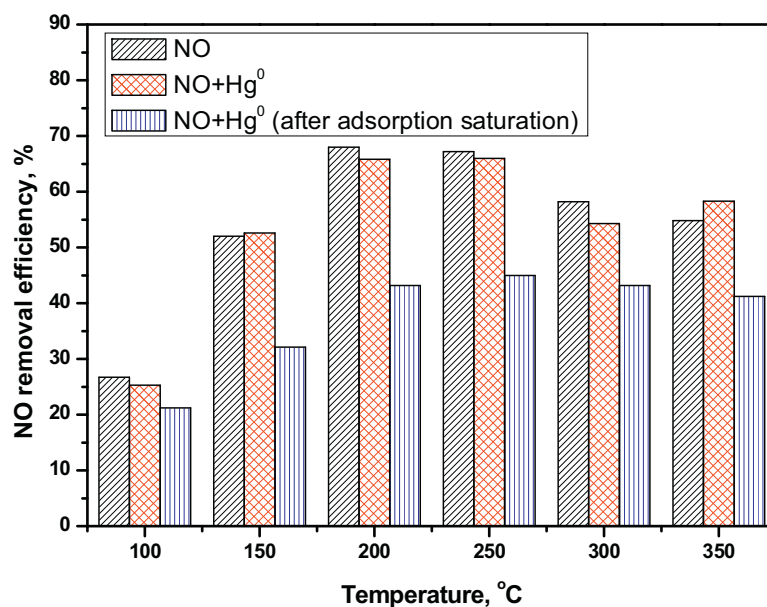


Fig. 5. The effect of Hg<sup>0</sup> on NO removal efficiency. (Reaction conditions: NO = NH<sub>3</sub> = 500 ppm, Hg<sup>0</sup> = 500 μg/m<sup>3</sup>, O<sub>2</sub> = 4%, GHSV = 478,000 h<sup>-1</sup> and N<sub>2</sub> as balance.).

temperature window (100–200 °C), it is beneficial for Hg<sup>0</sup> capture downstream from ESP or FF in the coal-fired power plants.

### 3.2.2. Hg<sup>0</sup> adsorption activity over LaMnO<sub>3</sub>

To investigate the role of the perovskite crystal structure on Hg<sup>0</sup> removal, the adsorption test was performed in a fix-bed adsorption system. As shown in Fig. 4(b), Hg<sup>0</sup> removal activity increased in the following order: LaO<sub>x</sub> < MnO<sub>x</sub> < LaMnO<sub>x</sub>. LaO<sub>x</sub> oxide exhibited almost no activity for Hg<sup>0</sup> removal. MnO<sub>x</sub> gradually lost its Hg<sup>0</sup> removal ability, and the Hg<sup>0</sup> removal efficiency was only approximately 30% after 600 min reaction. LaMnO<sub>3</sub> achieved the best performance with a Hg<sup>0</sup> removal efficiency that was higher than 85% after 600 min reaction. The saturation adsorption capacity of LaMnO<sub>3</sub> for Hg<sup>0</sup> was calculated to be approximately 7.65 mg/g. The effect of Hg<sup>0</sup> on NO removal was also investigated. As shown in Fig. 5, in the presence of Hg<sup>0</sup>, it existed a slight decrease for the removal of NO. But the trend was similar. It indicated that the addition of Hg<sup>0</sup> in the simulated gas had little effect on the NO removal. To further confirm the NO removal performance, the sample was first used for Hg<sup>0</sup> adsorption, and after adsorption saturation, the sample was used for NO removal. The NO removal efficiencies decreased sharply, especially at low temperature. Mn is most likely the main active site for Hg<sup>0</sup> removal based on previous reported results [29,31,33]. The high activity of LaMnO<sub>3</sub> was due to the benefit of perovskite crystal structure [34]. Mn<sup>n+</sup> exhibited a better dispersion in the perovskite structure where it was located in the B sites of the lattice. The highly dispersed Mn<sup>n+</sup> was beneficial for the Hg<sup>0</sup> catalytic oxidation on its surface [34]. Based on the characterization results, LaMnO<sub>3</sub> had the largest BET surface area, which was approximately 50% larger than that of MnO<sub>x</sub>. The larger surface area was beneficial for physical adsorption. However, the large surface area was not the primary reason for the higher Hg<sup>0</sup> removal efficiencies. In our previous studies, the BET surface areas of Mn-based materials were larger than LaMnO<sub>3</sub> [35,36]. Therefore, the perovskite structure of LaMnO<sub>3</sub> contributed to the high catalytic activity for Hg<sup>0</sup> removal.

The effects of the Hg<sup>0</sup> initial concentration, gas hourly space velocity (GHSV) and temperature were investigated. As shown in Fig. 6(a), the initial Hg<sup>0</sup> concentrations were set to 100, 300 and 500 μg/m<sup>3</sup>, respectively. When the initial Hg<sup>0</sup> concentration was 500 μg/m<sup>3</sup>, the Hg<sup>0</sup> removal efficiency was approximately 50%

after 600 min adsorption. However, when the initial Hg<sup>0</sup> concentration decreased to 300 μg/m<sup>3</sup>, the Hg<sup>0</sup> removal efficiency was higher than that at an initial Hg<sup>0</sup> concentration of 500 μg/m<sup>3</sup> after 600 min adsorption. When the initial Hg<sup>0</sup> concentration was further decreased to 100 μg/m<sup>3</sup>, the removal efficiency was maintained at a value higher than 95%. The effect of the GHSV was also investigated. The GHSV was set by changing the total gas flow rate. The GHSVs were 478,000, 286,800 and 95,600 h<sup>-1</sup> when the total flow rates were 500, 300 and 100 ml/min, respectively. As shown in Fig. 6(b), the Hg<sup>0</sup> removal efficiency increased when the GHSV decreased. The Hg<sup>0</sup> removal efficiency (after 600 min adsorption) was approximately 90% when the GHSV decreased to 95,600 h<sup>-1</sup>. To further investigate the Hg<sup>0</sup> removal mechanism over LaMnO<sub>3</sub> and the effects of the gas components, the reaction conditions were set to 500 μg/m<sup>3</sup> of inlet Hg<sup>0</sup> and GHSV = 478,000 h<sup>-1</sup> even though the removal efficiency was not high under this condition. The effect of temperature was also investigated, and the temperature window ranged from 100 to 300 °C. The Hg<sup>0</sup> capacities increased from 6.13 mg/g at 100 °C to 6.22 mg/g at 150 °C. However, when the temperature increased from 150 to 300 °C, the Hg<sup>0</sup> capacity decreased to only 3.01 mg/g at 300 °C. The higher temperature resulted in LaMnO<sub>3</sub> losing its performance for Hg<sup>0</sup> removal. Manganese oxides may exhibit better activity at low temperature [35,37]. Herein, to gain insight into the LaMnO<sub>3</sub> sorbents, the reaction temperature were set to 150 °C, the inlet concentration was 500 μg/m<sup>3</sup> and the GHSV was 478,000 h<sup>-1</sup>.

### 3.2.3. Effect of O<sub>2</sub> on Hg<sup>0</sup> adsorption

In general, the Hg<sup>0</sup> removal mechanism over Mn-based oxides involves the chemical adsorption. The catalytic oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup> enhanced the performance for Hg<sup>0</sup> capture. O<sub>2</sub> is the common oxidants of Hg<sup>0</sup> oxidation. Pure physical adsorption does not result in higher Hg<sup>0</sup> capacities. The adsorption experiments under pure N<sub>2</sub> were performed, and the results are shown in Fig. 7. LaMnO<sub>3</sub> exhibited a gradual decrease in its Hg<sup>0</sup> removal performance. After 125 min adsorption, the Hg<sup>0</sup> removal efficiency was only 50%. However, when 4% O<sub>2</sub> was added to the simulated gas, the Hg<sup>0</sup> removal efficiency increased. The existence of O<sub>2</sub> in the flue gas participated in the Hg<sup>0</sup> removal process. The Hg<sup>0</sup> removal experiments under pure N<sub>2</sub>, 4% O<sub>2</sub> and 8% O<sub>2</sub> during a 600 min reaction were further investigated. The Hg<sup>0</sup> adsorption capacities were calculated and are



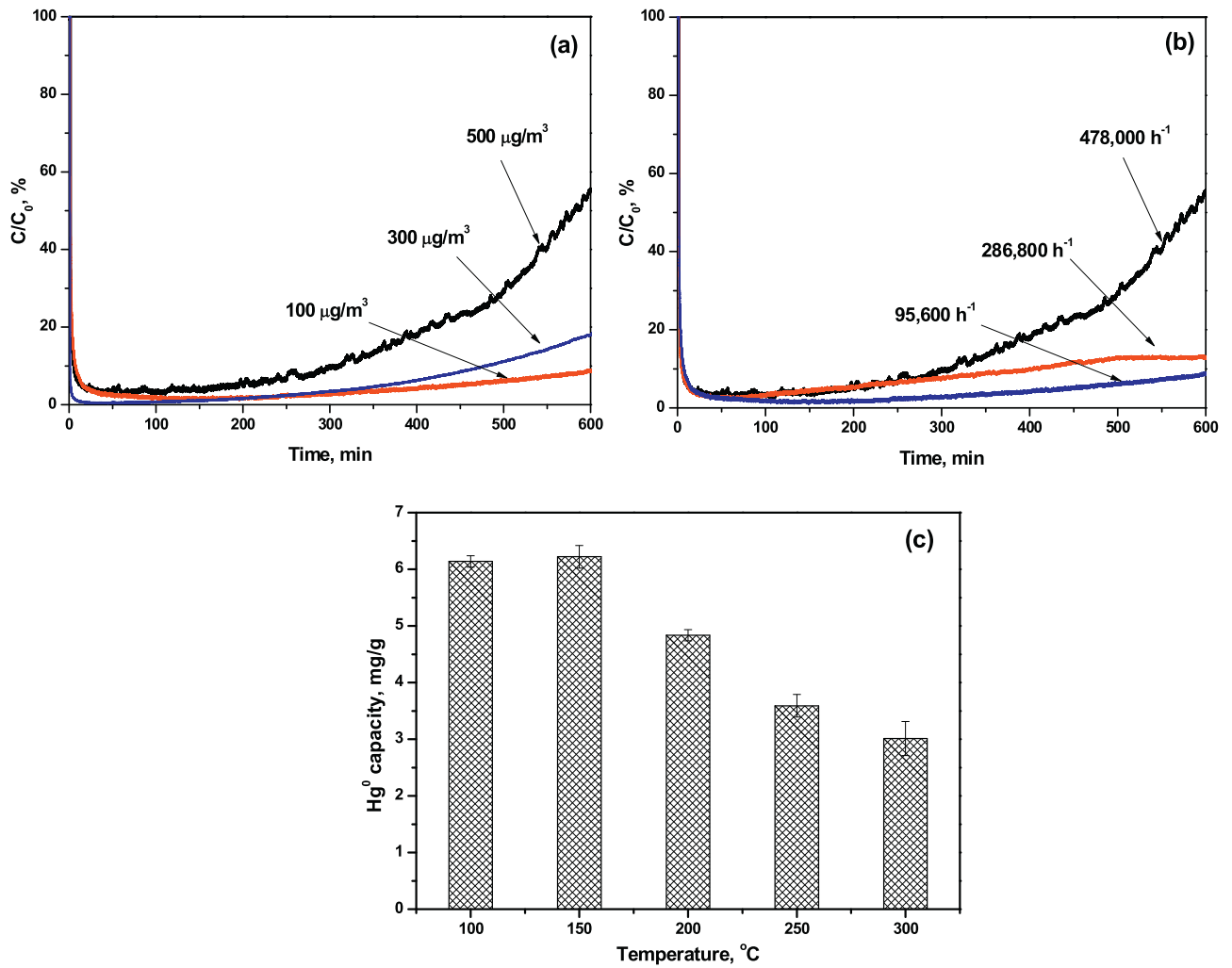


Fig. 6. (a) Effect of initial  $\text{Hg}^0$  concentration, (b) gas hourly space velocity (GHSV), and (c) temperature on  $\text{Hg}^0$  adsorption over  $\text{LaMnO}_3$ . Reaction condition: 4%  $\text{O}_2$ .

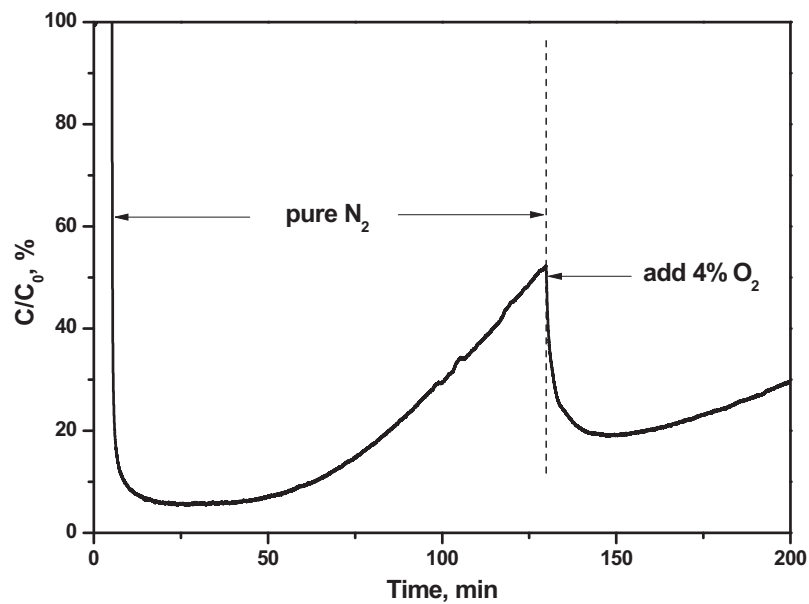


Fig. 7. Effect of  $\text{O}_2$  on  $\text{Hg}^0$  removal. Reaction condition:  $150^\circ\text{C}$ ;  $\text{GHSV} = 478,000 \text{ h}^{-1}$ ; 4%  $\text{O}_2$ .

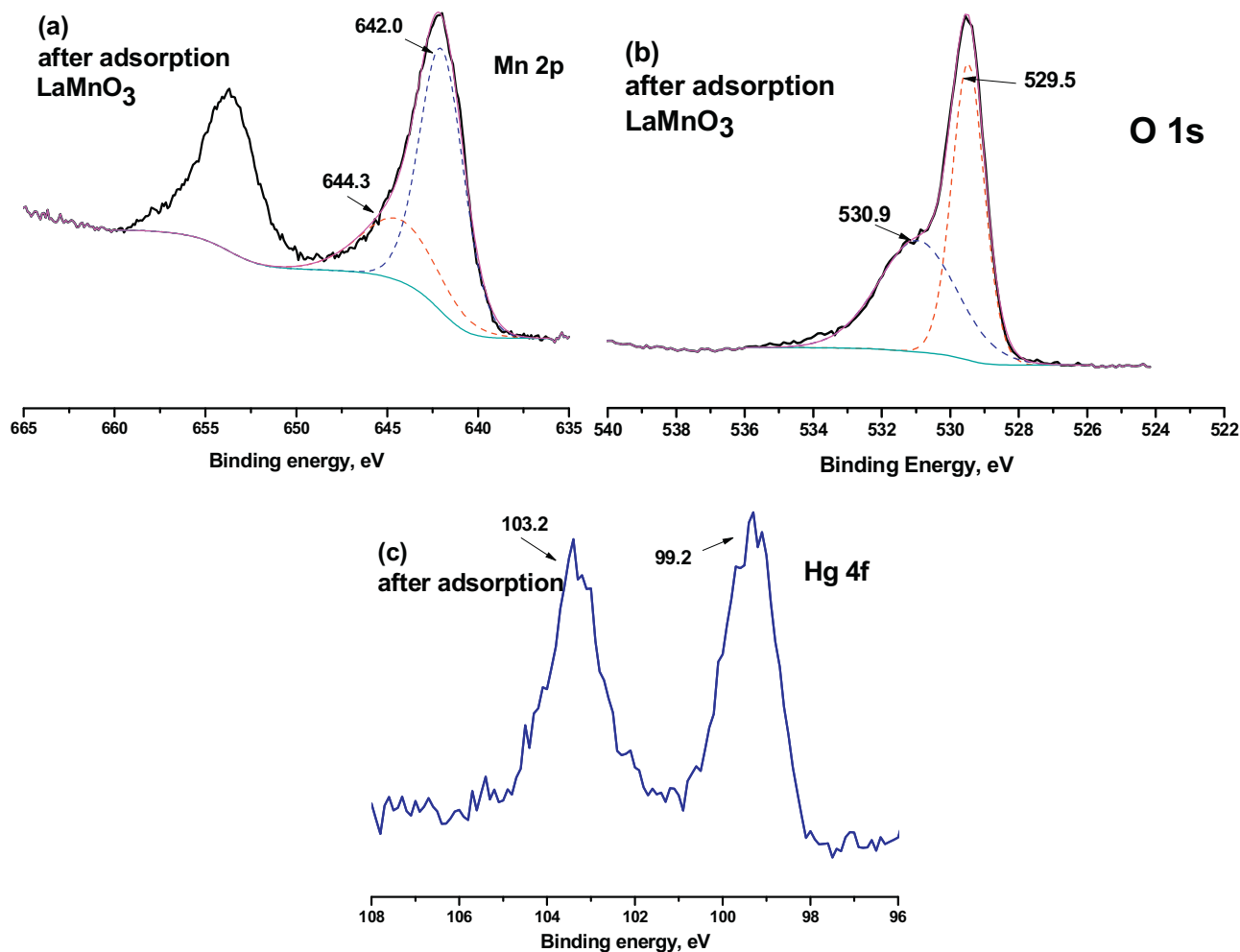


Fig. 8. XPS spectra of the LaMnO<sub>3</sub> sample after adsorption: (a) Mn 2p, (b) O 1s and (c) Hg 4f.

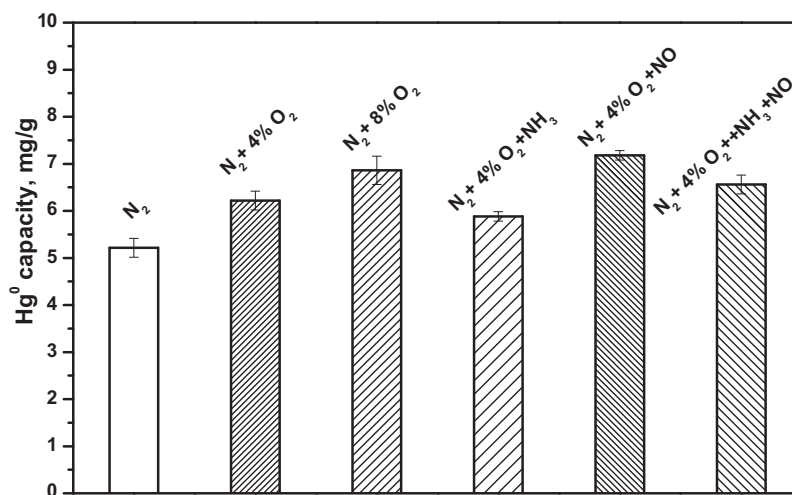


Fig. 9. Hg<sup>0</sup> capacities under pure N<sub>2</sub>, 4% O<sub>2</sub>, 8% O<sub>2</sub>, 4% O<sub>2</sub> + 500 ppm NH<sub>3</sub>, 4% O<sub>2</sub> + 500 ppm NO, and 4% O<sub>2</sub> + 500 ppm NO + 500 ppm NH<sub>3</sub>. Reaction condition: 150 °C and GHSV = 478000 h<sup>-1</sup>.

shown in Fig. 9, the Hg<sup>0</sup> capacity decreased by approximately 17% in the absence of O<sub>2</sub>. When the concentration of O<sub>2</sub> was increased to 8%, the Hg<sup>0</sup> capacities increased from 6.2 mg/g to approximately 6.8 mg/g. The H<sub>2</sub>-TPR profile of LaMnO<sub>3</sub> is shown in Fig. S2. The peaks centered at 330.5 (peak 1) and 741.1 °C (peak 2) were due

to the reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup> and Mn<sup>3+</sup> to Mn<sup>2+</sup>, respectively. The peak 1/peak 2 ratio was 56.8/43.2. The results indicated the boundaries between Mn<sup>4+</sup> to Mn<sup>3+</sup> and Mn<sup>3+</sup> to Mn<sup>2+</sup>.

After adsorption, the XPS spectra of Mn 2p, O 1s and Hg 4f were recorded, and the results are shown in Fig. 8. In the XPS spec-

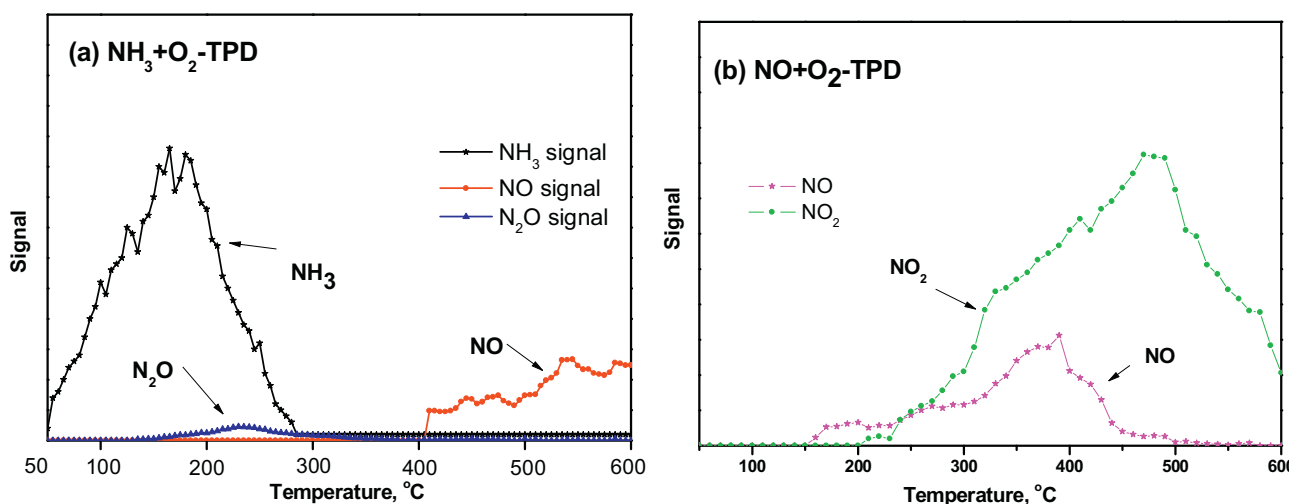
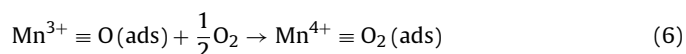
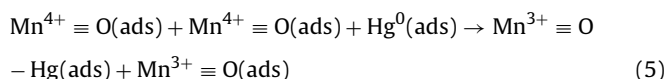


Fig. 10. (a)  $\text{NH}_3 + \text{O}_2$ -TPD, and (b)  $\text{NO} + \text{O}_2$ -TPD profiles over the  $\text{LaMnO}_3$  samples.

tra of Mn 2p shown in Fig. 8(a), the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  ratio changed to 29.14/70.86. A portion of the  $\text{Mn}^{4+}$  changed to  $\text{Mn}^{3+}$  during the adsorption process. After adsorption, (Fig. 8(b)), the  $\text{O}_{\text{latt}}/\text{O}_{\text{ads}}$  ratio was approximately 48.05/51.05, and the ratio decreased due to an increase in  $\text{O}_{\text{ads}}$  on the surface of  $\text{LaMnO}_3$ . The oxygen in the flue gas was first adsorbed on the surface of  $\text{LaMnO}_3$  to generate  $\text{O}_{\text{ads}}$ . This  $\text{O}_{\text{ads}}$  combined with  $\text{Hg}^0$  which was also adsorbed on the surface of  $\text{LaMnO}_3$ . To further confirm the results, the XPS spectrum of Hg 4f is shown in Fig. 8(c), and the peaks located at 103.2 and 99.2 eV were ascribed to  $\text{HgO}$ . The adsorbed  $\text{Hg}^0$  existed as  $\text{HgO}$  on the surface of  $\text{LaMnO}_3$ . The mechanism of  $\text{Hg}^0$  adsorption can be illustrated as follows:



### 3.2.4. Effect of $\text{NH}_3$ and $\text{NO}$ on $\text{Hg}^0$ removal

$\text{LaMnO}_3$  was used as the low temperature  $\text{NH}_3$ -SCR catalyst in previous studies. As shown in Fig. 9, the effects of  $\text{NH}_3$  and  $\text{NO}$  on the  $\text{Hg}^0$  adsorption capacities were presented. The reaction condition were 500 ppm  $\text{NH}_3$ , 500 ppm  $\text{NO}$ ,  $150^\circ\text{C}$  and a GHSV =  $478000 \text{ h}^{-1}$ .  $\text{NH}_3$  decreased the  $\text{Hg}^0$  capacity of  $\text{LaMnO}_3$ , and the  $\text{Hg}^0$  capacities decreased to 5.88 mg/g compared to 6.22 mg/g only under only 4%  $\text{O}_2$ . However,  $\text{NO}$  enhanced the  $\text{Hg}^0$  adsorption capacity, and the  $\text{Hg}^0$  capacity was 7.18 mg/g after 600 min of adsorption. When the gas component was 4%  $\text{O}_2$  + 500 ppm  $\text{NO}$  + 500 ppm  $\text{NH}_3$ , the  $\text{Hg}^0$  capacity decreased compared to that with 4%  $\text{O}_2$  + 500 ppm  $\text{NO}$  and increased compared to that with 4%  $\text{O}_2$  + 500 ppm  $\text{NH}_3$ .

To investigate the  $\text{NH}_3$  surface oxidation and  $\text{NO}$  oxidation performance,  $\text{NH}_3 + \text{O}_2$ -TPD and  $\text{NO} + \text{O}_2$ -TPD was performed in our study. A FT-IR gas analyzer was employed to detect the gas component along with the increase of temperature. As shown in Fig. 10(a), when the temperature increased from  $50^\circ\text{C}$ , the adsorbed  $\text{NH}_3$  started to release from the surface of  $\text{LaMnO}_3$ , and this  $\text{NH}_3$  was due to the physical-adsorbed  $\text{NH}_3$  (ad- $\text{NH}_3$ ) on the  $\text{LaMnO}_3$  surface. At a temperature of  $150^\circ\text{C}$ ,  $\text{N}_2\text{O}$  was detected. As the temperature increased to  $400^\circ\text{C}$ ,  $\text{NO}$  was released from the  $\text{LaMnO}_3$  surface. The ad- $\text{NH}_3$  may be oxidized to  $\text{N}_2\text{O}$  at low temperatures and  $\text{NO}$  at higher temperatures. The  $\text{NO} + \text{O}_2$ -TPD was also investigated

in this study. As shown in Fig. 10(b), the adsorbed- $\text{NO}$  (ad- $\text{NO}$ ) started to desorb from the surface of  $\text{LaMnO}_3$  at  $150^\circ\text{C}$ . As the temperature increased to  $200^\circ\text{C}$ ,  $\text{NO}_2$  started to release. The ad- $\text{NO}$  was most likely oxidized to  $\text{NO}_2$  by catalytic oxidation over  $\text{LaMnO}_3$ . The mechanism of  $\text{NH}_3$ -SCR reaction over  $\text{LaMnO}_3$  has been previously reported, especially for the reaction following the L-H mechanism [32,34]. It is unnecessary to distinguish the species on the  $\text{LaMnO}_3$  surface after  $\text{NH}_3/\text{NO}$  adsorption in previous studies based on DRIFTS studies. The desorbed  $\text{NH}_3$  can be assigned as ad- $\text{NH}_3$ , and the desorbed  $\text{NO}$  can be assigned to  $\text{NH}_3$  bond to acid sites [34]. Therefore, ad- $\text{NH}_3$  formed  $\text{NH}_4^+$  on the surface covered the active sites and consumed surface oxygen, which inhibited  $\text{Hg}^0$  oxidation, resulting in a low removal efficiency. However, the ad- $\text{NO}$  formed  $\text{NO}_2$  on the surface of  $\text{LaMnO}_3$ , and these species are most likely responsible for  $\text{Hg}^0$  oxidation [38].

### 3.2.5. Effect of $\text{SO}_2$ and $\text{H}_2$ on $\text{Hg}^0$ removal

The effects of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  on  $\text{Hg}^0$  removal were also investigated (Fig. 11).  $\text{SO}_2$  had an adverse effect on the  $\text{Hg}^0$  removal, and  $\text{Hg}^0$  capacity decreased approximately 20% when 500 ppm  $\text{SO}_2$  was included in the simulated gas.  $\text{SO}_2$  may easily react with Mn-based materials to form  $\text{Mn-SO}_4^{2-}$  [38,39].  $\text{NH}_3$  resulted in a decrease in the  $\text{Hg}^0$  capacity when  $\text{SO}_2$  was present, but  $\text{NO}$  promoted  $\text{Hg}^0$  removal even when  $\text{SO}_2$  was included in the simulated gas.  $\text{NH}_3$  can react with  $\text{SO}_2$  to form sulfate species, and causes catalyst deactivation. However, the existence of  $\text{H}_2\text{O}$  had an adverse effect on  $\text{Hg}^0$  adsorption, especially when  $\text{NH}_3$  and  $\text{NO}$  co-existed. Therefore,  $\text{NO}$  may form nitrate which results in a loss in oxidation performance. Furthermore, the active sites of  $\text{LaMnO}_3$  were occupied, resulting in low adsorption capacities. Moreover, the presence of both  $\text{SO}_2$  and  $\text{H}_2\text{O}$  had a serious adverse effect on  $\text{Hg}^0$  removal over  $\text{LaMnO}_3$ , and the  $\text{Hg}^0$  capacity was only 50% compare to that under  $\text{N}_2$  + 4% $\text{O}_2$ . When  $\text{NH}_3$  and  $\text{NO}$  were added to the simulated gas, the  $\text{Hg}^0$  adsorption capacity further decreased, and the capacity decreased to only 2.5 mg/g under 4%  $\text{O}_2$  + 4%  $\text{H}_2\text{O}$  + 500 ppm  $\text{NH}_3$  + 500 ppm  $\text{NO}$  + 500 ppm  $\text{SO}_2$ . It is interesting to further discuss the mechanism for the interaction among the  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{NO}$  (Fig. 11).

### 3.3. Mercury temperature-programmed-desorption ( $\text{Hg}$ -TPD)

The mercury temperature-programmed-desorption ( $\text{Hg}$ -TPD) method was performed. In addition, the desorption activation energy ( $E_d$ ) was calculated to explain the binding force between mercury and  $\text{LaMnO}_3$ . The adsorption under different gas atmo-



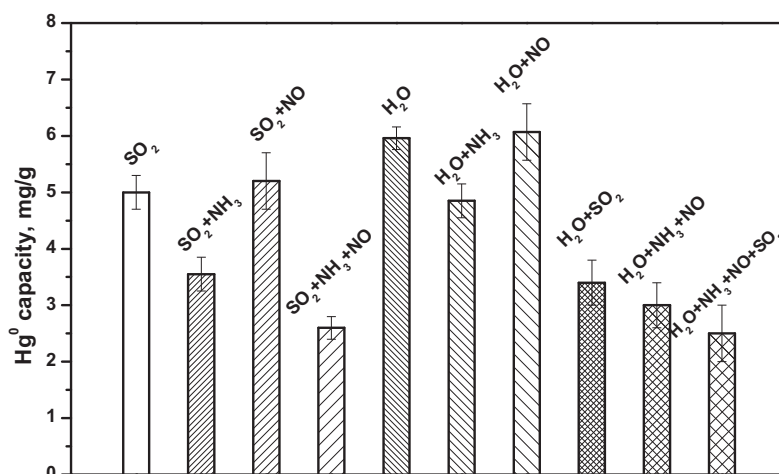


Fig. 11. Effects of SO<sub>2</sub> and H<sub>2</sub>O on the Hg<sup>0</sup> adsorption capacity. Reaction condition: 150 °C; GHSV = 478,000 h<sup>-1</sup>; O<sub>2</sub>: 4%; NH<sub>3</sub>: 500 ppm; NO: 500 ppm; SO<sub>2</sub>: 500 ppm; H<sub>2</sub>O: 4%.

sphere and desorption under pure N<sub>2</sub> was first studied. The Hg-TPD model for the  $E_d$  calculation was as follows:

The Hg<sup>0</sup> desorption process was assumed as to follow first-order kinetics [40–42]:

$$\frac{r_d}{N_s} = -\frac{d\theta}{dt} = k_d\theta \quad (7)$$

where  $r_d$  is the desorption rate of mercury from the sorbent (mol/min),  $N_s$  is the maximum mercury concentration on the unit surface of the sorbent (mol/cm<sup>2</sup>),  $\theta$  is the transient coverage of mercury,  $t$  is the time (min) and  $k_d$  is the desorption rate.

Based on Eq. (7), the related parameters can be defined as follows:

$$k_d = A \exp\left(-\frac{E_d}{RT}\right) \quad (8)$$

$$\frac{r_d}{N_s} = -\frac{d\theta}{dt} = A\theta \exp\left(-\frac{E_d}{RT}\right) \quad (9)$$

$$T = T_0 + \beta t \quad (10)$$

where  $R$  is the gas constant,  $T$  is the temperature,  $A$  is the pre-exponential factor,  $\beta$  (K/min) is the heating rate and  $T_0$  (K) is the initial temperature of TPD experiment. Assuming that the desorption rate reaches a maximum value at a certain temperature  $T_p$  (K), then  $dr_d/dt = 0$ , and Eq. (7) can be expressed as follows:

$$2\ln T - \ln \beta = \frac{E_d}{RT_p} + \ln \frac{E_d}{AR} \quad (11)$$

Based on Eq. (11), the Hg-TPD curves under different heating rates are created by plotting of  $(2\ln T_p - \ln \beta)$  as a function of  $1/T_p$ , which generates a linear relationship, and  $E_d$  can be calculated.

First, the Hg-TPD experiments were performed using different gas components. N<sub>2</sub> + Hg-TPD, O<sub>2</sub> + Hg-TPD, NH<sub>3</sub> + O<sub>2</sub> + Hg-TPD, NO + O<sub>2</sub> + Hg-TPD and SO<sub>2</sub> + O<sub>2</sub> + Hg-TPD were tested. As shown in Fig. 12, the adsorption under pure N<sub>2</sub> resulted in two peaks. One peak located at approximately 248.5 °C was due to physical-adsorption on the LaMnO<sub>3</sub> surface. The primary desorption peak at approximately 342.5 °C may be associated with chemical-adsorption. For adsorption under 4% O<sub>2</sub>, the desorption peak was located at 361.5 °C which is higher than the second peak under N<sub>2</sub>. Based on Equation (8), as the desorption temperature increased, the desorption energy increased. For adsorption under NH<sub>3</sub> + O<sub>2</sub> and NO + O<sub>2</sub>, the primary desorption peaks were centered at 345.5 and 356.5 °C, respectively. The desorption peaks under O<sub>2</sub>, NH<sub>3</sub> + O<sub>2</sub> and NO + O<sub>2</sub> adsorption atmosphere were similar. However, for adsorption under SO<sub>2</sub> + O<sub>2</sub>, desorption began at approximately 230 °C,

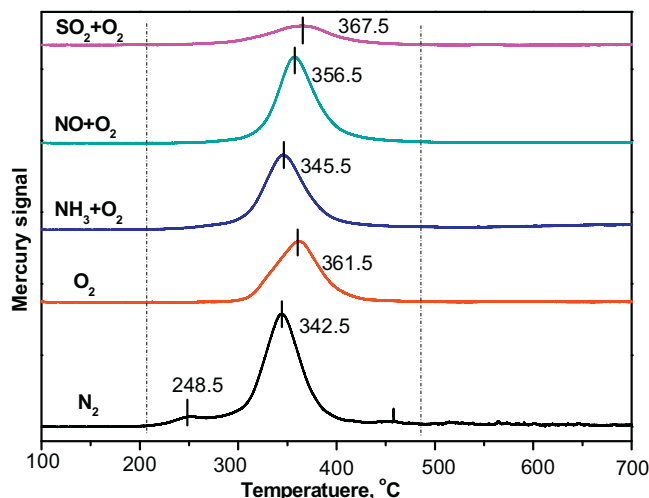


Fig. 12. Hg-TPD curves for LaMnO<sub>3</sub> under different adsorption conditions.

which is lower than that of under an O<sub>2</sub> atmosphere. In addition, a wide peak was observed in the curve of under SO<sub>2</sub> + O<sub>2</sub>. The sulfate (SO<sub>4</sub><sup>2-</sup>) on LaMnO<sub>3</sub> surface may have affected the Hg-O binding energy. The desorption energy based on Eq. (8) was calculated, and the O<sub>2</sub> + Hg-TPD for a desorption rate of 2, 5 and 10 °C/min is shown in Fig. S3. The desorption activation energy was 150.50 kJ/mol. LaMnO<sub>3</sub> can be regenerated by thermal desorption. The sample was re-used for Hg<sup>0</sup> adsorption, as shown in Fig. S4, and the Hg<sup>0</sup> capacities were nearly the same after the 5th adsorption run. The results indicated that LaMnO<sub>3</sub> can be fully regenerated.

Based on these results, the optimal reaction temperature for NO conversion is 200–250 °C and Hg<sup>0</sup> adsorption is 100–150 °C. In coal-fired power plants, the catalyst can be used downstream of ESP/FF, and in this section, the temperature is approximately 200 °C. A low-temperature NH<sub>3</sub>-SCR catalyst was also used in this section. LaMnO<sub>3</sub> had a NO removal efficiency of approximately 60–70% and a higher Hg<sup>0</sup> capacity. In a traditional coal-fired power plant, the NO concentration decreases after the SCR reaction, and the Hg<sup>0</sup> concentration also decreased after the SCR catalyst and ESP/FF. Therefore, the low-temperature NH<sub>3</sub>-SCR reactor may also be beneficial for simultaneous removal of Hg<sup>0</sup> and NO.

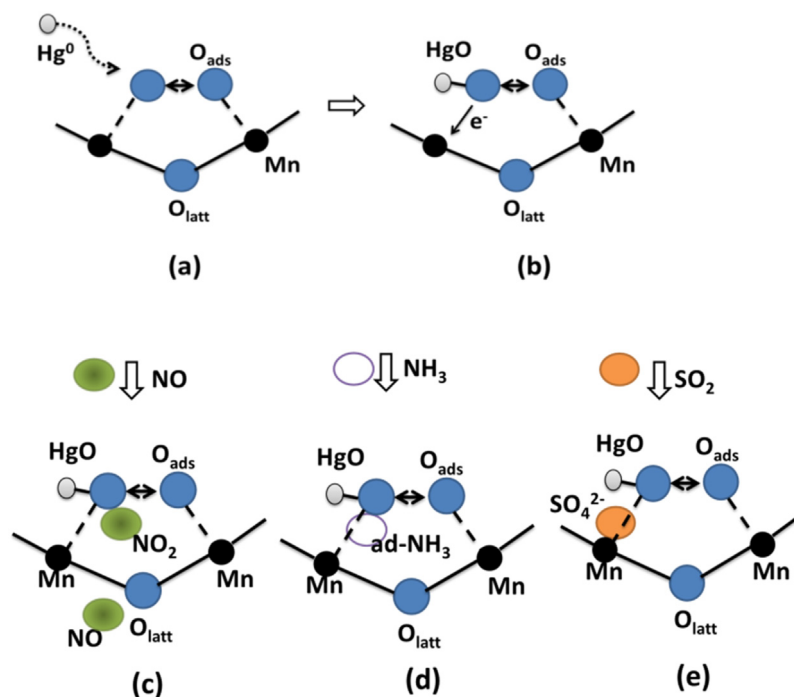


Fig. 13. Proposed reaction mechanism for  $\text{Hg}^0$  adsorption under different gas compositions over  $\text{LaMnO}_3$ .

#### 4. Conclusions

In this study,  $\text{LaMnO}_3$  perovskite oxide, which was used as a low-temperature  $\text{NH}_3$ -SCR catalyst, was confirmed to be a  $\text{Hg}^0$  sorbent. The perovskite structure was beneficial for  $\text{Hg}^0$  catalytic oxidation and adsorption, and the reduction of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  results in oxidation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$ . The adsorbed oxygen combined with  $\text{Hg}^{2+}$  to form  $\text{HgO}$  species on the  $\text{LaMnO}_3$  surface. The adsorption mechanism is briefly illustrated in Fig. 13, the  $\text{Hg}^0$  first adsorbed on  $\text{LaMnO}_3$  surface, then  $\text{Hg}^0$  was oxidized to  $\text{Hg}^{2+}$  and existed as  $\text{HgO}$  species. In addition, the existence of  $\text{NO}$  enhanced the  $\text{Hg}^0$  capacity but the presence of  $\text{NH}_3$  inhibited  $\text{Hg}^0$  adsorption.  $\text{NO}$  adsorption on  $\text{LaMnO}_3$  may result in the formation of  $\text{NO}_2$ , which is favorable for  $\text{Hg}^0$  oxidation. However, the existence of  $\text{ad-NH}_3$  occupied the adsorbed oxygen, resulting in difficulties with  $\text{Hg-O}$  bonding. The existence of  $\text{SO}_2$  also decreased the  $\text{Hg}^0$  capacity due to the sulfate generated on the  $\text{LaMnO}_3$  surface. A further improvement in the  $\text{LaMnO}_3$  materials is currently underway.  $\text{LaMnO}_3$  exhibited superior performance for  $\text{Hg}^0$  adsorption and is an ideal material for the simultaneous removal of  $\text{Hg}^0$  and  $\text{NO}$  at low-temperatures in coal-fired power plants.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.12.042>.

#### References

- [1] W.H. Schroeder, J. Munthe, *Atmos. Environ.* 32 (1998) 809–822.
- [2] N. Pirrone, P. Costa, J. Pacyna, R. Ferrara, *Atmos. Environ.* 35 (2001) 2997–3006.
- [3] K.-H. Kim, V.K. Mishra, S. Hong, *Atmos. Environ.* 40 (2006) 3281–3293.
- [4] Z.-W. Wang, Z.-S. Chen, D. Ning, X.-S. Zhang, *J. Environ. Sci.* 19 (2007) 176–180.
- [5] D.G. Streets, J. Hao, Y. Wu, J. Jiang, M. Chan, H. Tian, X. Feng, *Atmos. Environ.* 39 (2005) 7789–7806.
- [6] H. Kamata, S.-I. Ueno, T. Naito, A. Yukimura, *Ind. Eng. Chem. Res.* 47 (2008) 8136–8141.
- [7] M. Díaz-Somoano, S. Unterberger, K.R. Hein, *Fuel Proc. Technol.* 88 (2007) 259–263.
- [8] Y. Eom, S.H. Jeon, T.A. Ngo, J. Kim, T.G. Lee, *Catal. Lett.* 121 (2008) 219–225.
- [9] R.D. Vidic, D.P. Siler, *Carbon* 39 (2001) 3–14.
- [10] W. Liu, R.D. Vidic, T.D. Brown, *Environ. Sci. Technol.* 34 (2000) 483–488.
- [11] J. Wo, M. Zhang, X. Cheng, X. Zhong, J. Xu, X. Xu, *J. Hazard. Mater.* 172 (2009) 1106–1110.
- [12] S.J. Lee, Y.-C. Seo, J. Jurng, T.G. Lee, *Atmos. Environ.* 38 (2004) 4887–4893.
- [13] Z. Shen, J. Ma, Z. Mei, J. Zhang, *J. Environ. Sci.* 22 (2010) 1814–1819.
- [14] M.H. Kim, S.-W. Ham, J.-B. Lee, *Appl. Catal. B: Environ.* 99 (2010) 272–278.
- [15] Y. Li, P.D. Murphy, C.-Y. Wu, K.W. Powers, J.-C.J. Bonzongo, *Environ. Sci. Technol.* 42 (2008) 5304–5309.
- [16] B. Thirupathi, P.G. Smirniotis, *J. Catal.* 288 (2012) 74–83.
- [17] Y.J. Kim, H.J. Kwon, I. Heo, I.-S. Nam, B.K. Cho, J.W. Choung, M.-S. Cha, G.K. Yeo, *Appl. Catal. B: Environ.* 126 (2012) 9–21.
- [18] J. Li, H. Chang, L. Ma, J. Hao, R.T. Yang, *Catal. Today* 175 (2011) 147–156.
- [19] S. Straube, T. Hahn, H. Koeser, *Appl. Catal. B: Environ.* 79 (2008) 286–295.
- [20] Y. Gao, Z. Zhang, J. Wu, L. Duan, A. Umar, L. Sun, Z. Guo, Q. Wang, *Environ. Sci. Technol.* 47 (2013) 10813–10823.
- [21] Y. Nishihata, J. Mizuki, T. Akao, H. Tanaka, M. Uenishi, M. Kimura, T. Okamoto, N. Hamada, *Nature* 418 (2002) 164–167.
- [22] J. Suntivich, K.J. May, H.A. Gasteiger, J.B. Goodenough, Y. Shao-Horn, *Science* 334 (2011) 1383–1385.
- [23] Y. Teraoka, K. Kanada, S. Kagawa, *Appl. Catal. B-Environ.* 34 (2001) 73–78.
- [24] R. Spinicci, A. Tofanari, M. Faticanti, I. Pettiti, P. Porta, *J. Mol. Catal. A-Chem.* 176 (2001) 247–252.
- [25] C. Tofan, D. Klvan, J. Kirchnerova, *Appl. Catal. B-Environ.* 36 (2002) 311–323.
- [26] B. Tang, J. Ge, C. Wu, L. Zhuo, J. Niu, Z. Chen, Z. Shi, Y. Dong, *Nanotechnology* 15 (2004) 1273.
- [27] J. Chen, M. Shen, X. Wang, G. Qi, J. Wang, W. Li, *Appl. Catal. B: Environ.* 134–135 (2013) 251–257.
- [28] J. Li, N. Yan, Z. Qu, S. Qiao, S. Yang, Y. Guo, P. Liu, J. Jia, *Environ. Sci. Technol.* 44 (2009) 426–431.
- [29] C. He, B. Shen, J. Chen, J. Cai, *Environ. Sci. Technol.* 48 (2014) 7891–7898.
- [30] N. Russo, D. Fino, G. Saracco, V. Specchia, *J. Catal.* 229 (2005) 459–469.
- [31] H. Xu, Z. Qu, C. Zong, W. Huang, F. Quan, N. Yan, *Environ. Sci. Technol.* (2015).
- [32] R. Zhang, N. Luo, W. Yang, N. Liu, B. Chen, *J. Mol. Catal. A: Chem.* 371 (2013) 86–93.
- [33] H. Li, C.-Y. Wu, Y. Li, J. Zhang, *Appl. Catal. B: Environ.* 111 (2012) 381–388.

- [34] R. Zhang, W. Yang, N. Luo, P. Li, Z. Lei, B. Chen, *Appl. Catal. B: Environ.* 146 (2014) 94–104.
- [35] H. Xu, J. Xie, Y. Ma, Z. Qu, S. Zhao, W. Chen, W. Huang, N. Yan, *Fuel* 140 (2015) 803–809.
- [36] H. Xu, Z. Qu, S. Zhao, J. Mei, F. Quan, N. Yan, *J. Hazard. Mater.* 299 (2015) 86–93.
- [37] J. Xie, H. Xu, Z. Qu, W. Huang, W. Chen, Y. Ma, S. Zhao, P. Liu, N. Yan, *J. Colloid Interface Sci.* 428 (2014) 121–127.
- [38] H. Li, C.-Y. Wu, Y. Li, L. Li, Y. Zhao, J. Zhang, *J. Hazard. Mater.* 243 (2012) 117–123.
- [39] S. Yang, Y. Guo, N. Yan, D. Wu, H. He, J. Xie, Z. Qu, J. Jia, *Appl. Catal. B: Environ.* 101 (2011) 698–708.
- [40] H.X. Xi, Z. Li, H.B. Zhang, X. Li, X.J. Hu, *Sep. Purif. Technol.* 31 (2003) 41–45.
- [41] Z. Li, H.J. Wang, H.X. Xi, Q.B. Xia, J.L. Han, L.A. Lu, *Adsorpt. Sci. Technol.* 21 (2003) 125–133.
- [42] R.T. Yang, R.Q. Long, J. Padin, A. Takahashi, T. Takahashi, *Ind. Eng. Chem. Res.* 38 (1999) 2726–2731.